

## LETTERS TO THE EDITOR

The Letters to the Editor section is divided into three categories entitled Notes, Comments, and Errata. Letters to the Editor are limited to one and three-fourths journal pages as described in the Announcement in the 1 January 2003 issue.

## COMMENTS

## Comment on "Atomization energies and enthalpies of formation of the $\text{SnBi}_n$ ( $n=1-3$ ) gaseous molecules by Knudsen cell mass spectrometry" [J. Chem. Phys. 116, 6957 (2002)]

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In their paper,<sup>1</sup> Meloni and Gingerich reported on preliminary theoretical results by our group (Sec. 3 and Ref. 24). We want to add relevant information here (a) on the structure of the  $\text{SnBi}_2$  molecule, and (b) on our computed atomization energies for  $\text{SnBi}_n$  ( $n=1-3$ ).

Table I shows geometries optimized in density-functional calculations using the B3LYP functional<sup>2</sup> together with our large-core relativistic effective-core potentials (ECPs)<sup>3</sup> and corresponding  $[4s4p3d2f]$  valence basis sets.<sup>3,4</sup> It is to be noted that  $\text{SnBi}_2$  has  $C_{2v}$  equilibrium structure which is lower in energy by  $\sim 154$  kJ/mol [as obtained in single-point coupled-cluster calculations with single and double excitations and perturbative account of triples (CCSD(T)] than the  $D_{\infty h}$  geometry reported by Meloni and Gingerich.

Also shown in Table I are atomization energies with respect to separate ground-state atoms, evaluated in single-point calculations at the above-discussed geometries. In an attempt to gradually improve on the accuracy of the large-core-ECP B3LYP values, we first replaced the large-core ECPs (and the  $[4s4p3d2f]$  valence basis sets) by small-core ECPs<sup>5</sup> (and corresponding  $[7s7p5d3f2g]$  basis sets<sup>4</sup>), and changed from B3LYP to CCSD(T), in a second step. While our best result for  $\text{SnBi}$  lies at the upper end of the experimental error bars, significant deviations from experiment are found for  $\text{SnBi}_2$  and  $\text{SnBi}_3$ , of  $\sim 65$  and  $\sim 100$  kJ/mol, respectively. Basis-set superposition errors cannot be responsible for these deviations since counterpoise (CP) corrections<sup>6</sup> to the CCSD(T) values amount to only 0.5 and 1.4 kJ/mol for  $\text{SnBi}$  and  $\text{SnBi}_2$ , respectively. Also, zero-point energies (not included in the atomization energies of Table I) have small effect (3 kJ/mol for  $\text{SnBi}_2$ , 4 kJ/mol for  $\text{SnBi}_3$ ). On the other hand, correlation contributions from the outer-core  $d$  shells of Sn and Bi, also not included in the

CCSD(T) values of Table I, increase our atomization energies by 10 kJ/mol for  $\text{SnBi}$  and 23 kJ/mol for  $\text{SnBi}_2$  [CCSD(T) level, CP corrected], thus enhancing the difference to experiment. The role of spin-orbit (SO) contributions can be estimated by using the large-core SO-ECPs in full-valence complete active space self-consistent field calculations (active orbitals optimized for [state-averages of degenerate] atomic/molecular ground states, SO matrix elements generated for all states with at most one electron outside the strongly occupied ground-state orbitals); we obtain a reduction of the atomization energy by 5 kJ/mol for  $\text{SnBi}$ , and by 55 kJ/mol for  $\text{SnBi}_2$ . Still, our best estimates [cf. Table I, CCSD(T)-SO, including outer-core correlation] are outside the experimental error bars. All the calculations

TABLE I.  $\text{SnBi}_n$  bond lengths (in Å) and atomization energies (in kJ/mol).

	$\text{SnBi}$ , <sup>2</sup> I	$\text{SnBi}_2$ , <sup>1</sup> A <sub>1</sub>	$\text{SnBi}_3$ , <sup>2</sup> A'
$r(\text{Sn-Bi})^a$	2.70	2.88	2.95 (2×), 3.28
$r(\text{Bi-Bi})^a$	...	2.81	2.93 (2×), 3.10
$\Delta E_{\text{at,B3LYP}}^b$	235	543	791
$\Delta E_{\text{at,B3LYP}}^c$	230	513	736
$\Delta E_{\text{at,CCSD(T)}}^d$	204	480	700
$\Delta E_{\text{at,CCSD(T)-SO}}^e$	209	448	
$\Delta E_{\text{at,exp}}^f$	$191.1 \pm 12.0$	$415.2 \pm 15.0$	$603.4 \pm 18.0$

<sup>a</sup>Bond lengths optimized at B3LYP level using large-core ECPs and  $[4s4p3d2f]$  basis sets ( $[4s4p3d]$  in the case of  $\text{SnBi}_3$ ).

<sup>b</sup>B3LYP atomization energies with large-core ECPs and  $[4s4p3d2f]$  basis sets, evaluated at the geometries listed above.

<sup>c</sup>Same as (b), but small-core ECPs and  $[7s7p5d3f2g]$  basis sets used.

<sup>d</sup>Same as (c), but atomization energies evaluated at CCSD(T) level [without excitations from the outer-core ( $n-1$ ) $spd$  shells].

<sup>e</sup>Same as (d), but corrections for effects of spin-orbit coupling and outer-core correlation included (cf. the text).

<sup>f</sup>Experimental values from Ref. 1.

of this work have been done using the MOLPRO<sup>7</sup> suite of programs.

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<sup>1</sup>G. Meloni and K. A. Gingerich, *J. Chem. Phys.* **116**, 6957 (2002).

<sup>2</sup>A. D. Becke, *J. Chem. Phys.* **98**, 5648 (1993).

<sup>3</sup>H. Stoll, B. Metz, and M. Dolg, *J. Comput. Chem.* **23**, 767 (2002).

<sup>4</sup>K. A. Peterson (unpublished).

<sup>5</sup>B. Metz, H. Stoll, and M. Dolg, *J. Chem. Phys.* **113**, 2563 (2000).

<sup>6</sup>S. F. Boys and F. Bernardi, *Mol. Phys.* **19**, 203 (1970).

<sup>7</sup>MOLPRO is a package of *ab initio* programs designed by H.-J. Werner and P. J. Knowles, version 2002.1, R. D. Amos, A. Bernhardsson, A. Berning *et al.*; C. Hampel, K. Peterson, and H.-J. Werner, *Chem. Phys. Lett.* **190**, 1 (1992); M. J. O. Deegan and P. J. Knowles, *ibid.* **227**, 321 (1994); P. J. Knowles, C. Hampel, and H.-J. Werner, *J. Chem. Phys.* **99**, 5219 (1993); **112**, 3106 (2000); A. Berning, M. Schweizer, H.-J. Werner, P. J. Knowles, and P. Palmieri, *Mol. Phys.* **98**, 1823 (2000).